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11-24-03  
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TC 1700

Our Case No. 5404/15

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Masahiro Ueda et al.

Serial No. 10/018,905

Filing Date: December 17, 2001

Title: REGENERATED COLLAGEN  
FIBER REDUCED IN ODOR AND  
IMPROVED IN SUITABILITY FOR  
SETTING, PROCESS FOR  
PRODUCING THE SAME, AND  
METHOD OF SETTING

Examiner: Margaret V. Einsmann

Group Art Unit No.: 1751

## LETTER OF TRANSMITTAL--CERTIFIED TRANSLATIONS OF PRIORITY APPLICATIONS

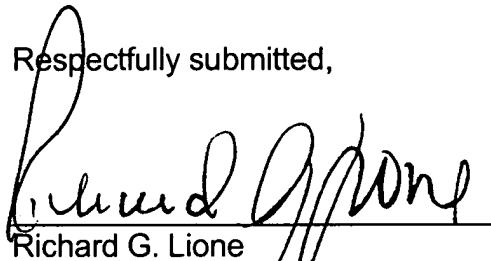
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

Transmitted herewith are certified copies of English translations for Japanese Patent Application Nos. 179328/1999 and 191859/1999, the two priority applications for

the above-identified U.S. application. It is requested that they be entered in the U.S. application.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Richard G. Lione", is written over a horizontal line.

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# VERIFICATION OF TRANSLATION

I, Fumio Akiyama, being a citizen of Japan, residing at c/o ASAHINA & CO., NS Bldg., No. 2-22, Tanimachi 2-chome, Chuo-ku, Osaka-shi, Osaka, 540-0012, Japan, do solemnly and sincerely declare as follows:

I am a translator, of ASAHINA & CO., of NS Bldg., No. 2-22, Tanimachi 2-chome, Chuo-ku, Osaka, 540-0012, Japan.

I am well acquainted with the English and Japanese languages.

The attached translation is a true and correct translation into the English language of a certified copy of Japanese Patent Application No. 179328/1999 filed on June 25, 1999.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 17th day of November, 2003

by Fumio Akiyama

Fumio Akiyama

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: June 25, 1999

Application Number: 179328/1999

Applicant(s): KANEKA CORPORATION

July 28, 2000

Commissioner, Patent Office      Kozo Oikawa

Appln. Certification No. Pat. 2000-3058434

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[To whom]	Commissioner of Patent Office
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[Material name]	Specification	1
[Material name]	Abstract	1
[Necessity of proof]	Necessary	

[Document Name]

SPECIFICATION

[Title of the Invention]

REGENERATED COLLAGEN FIBER IMPROVED IN  
SUITABILITY FOR SETTING AND PROCESS FOR  
PRODUCING THE SAME

[CLAIMS]

1. A regenerated collagen fiber which is obtained by treating collagen with a monofunctional epoxy compound and an aluminum salt.

2. The regenerated collagen fiber of Claim 1, wherein said monofunctional epoxy compound is a compound represented by the following formula (I):



(in which R indicates a substituent group represented by  $\text{R}_1-$ ,  $\text{R}_2-\text{O}-$  or  $\text{R}_2-\text{COO}-$ ,  $\text{R}_1$  in said substituent group indicates a hydrocarbon group having at least 2 carbon atoms or  $\text{CH}_2\text{Cl}$  and  $\text{R}_2$  indicates a hydrocarbon group having at least 4 carbon atoms).

3. The regenerated collagen fiber of Claim 2, wherein said  $\text{R}_1$  in the formula indicates a hydrocarbon group having at least 2 and at most 6 carbon atoms or  $\text{CH}_2\text{Cl}$  and  $\text{R}_2$  indicates a hydrocarbon group

having at least 4 and at most 6 carbon atoms.

4. The regenerated collagen fiber of Claim 1, 2 or 3, wherein said aluminum salt is basic aluminum chloride or basic aluminum sulfate represented by the following formula (II) and (III):



(wherein n is 0.5 to 2.5).

5. A process for preparing regenerated collagen fiber which comprises treating collagen with a monofunctional epoxy compound, and then treating the same with an aluminum salt in such a way that 2 to 20 % by weight of an aluminum salt converted to an aluminum oxide basis is contained to said collagen.

6. A process for setting a regenerated collagen fiber which comprises thermally setting the regenerated collagen fiber of Claim 1 by means of hot water treatment at 20° to 160°C and heat drying treatment at 60° to 220°C.

#### [DETAILED DESCRIPTION OF THE INVENTION]

##### [Technical Field of the Invention]

The present invention relates to regenerated collagen fibers improved in suitability for setting. More specifically, the present



invention relates to regenerated collagen fibers which has no color and excellent touch in wet conditions, which can be formed into a desirable shape easily with the shape being maintained properly. Such regenerated collagen fibers can be suitably used for curling hair ornaments such as wigs, hairpieces and doll hair or for shaping (setting) textile goods comprising woven fabrics or non-woven fabrics.

[Prior Art]

To make regenerated collagen fibers water-resistant with no color, there are processes for treating collagen fibers with metallic salt such as aluminum salt or zirconium salt as disclosed in Japanese Unexamined Patent Publication No. 50370/1992, Japanese Unexamined Patent Publication No. 173161/1994 and Japanese Unexamined Patent Publication No. 308221/1992, and a process for treating collagen fibers with an epoxy compound as disclosed in Japanese Unexamined Patent Publication No. 352804/1992. As a process for shaping regenerated collagen fibers, a process disclosed in Japanese Unexamined Patent Publication No. 333660/1992 or Japanese Unexamined Patent Publication No. 250081/1997 which comprises moisturizing fibers in warm water or an aqueous solution containing monovalent or divalent cationic hydrosulfate, and heat-treating the fibers is known. However, when the regenerated collagen fibers which are made water-resistant by the treatment with metallic salt such as aluminum salt or zirconium salt are shaped according to the above method, shape keeping ability (set property) thereof is extremely low though certain shape can be given to the fibers. Furthermore, the given shape is lost immediately when water washing (including shampoo washing) and drying are repeated. Thus, it was difficult to use these

fibers for hair products such as wigs, hairpieces and doll hair. Additionally, in case of using a multivalent alcohol, i.e., glycidyl ether which is regarded as the most preferable compound among epoxy compounds described in Japanese Unexamined Patent Publication No. 352804/1992, fibers became brittle and hard, and strength thereof was remarkably lost, causing problems during production process of hair ornament, for example, hair implant or sewing machine operation.

[Problems to be Solved by the Invention]

An object of the present invention is to provide regenerated collagen fibers which have no color and excellent touch in wet conditions, which can be formed into a desirable shape easily and whose setting can be carried out with maintaining the shape properly.

[Means to Solve the Problem]

As a result of intensive research by the present inventors in view of the current conditions mentioned above, the present invention has been completed based on the findings that it is possible to obtain regenerated collagen fibers which have natural light color of collagen, improved hardness when the fibers are wet, and excellent touch in wet conditions by combining two kinds of treatment, namely, treatment by a monofunctional epoxy compound and treatment by an aluminum salt.

The regenerated collagen fibers of the present invention are regenerated collagen fibers which are obtained by treating collagen with a monofunctional epoxy compound and an aluminum salt. The process for preparing the regenerated collagen fibers comprises treating collagen with a monofunctional epoxy compound and then treating the same with an aluminum salt in such a way that 2 to 20 % by weight of an aluminum salt converted to an aluminum oxide basis is contained to

said collagen.

The process for setting of the present invention is a process for setting which comprises thermally setting the regenerated collagen fibers by means of hot water treatment at 20° to 160°C and heat drying treatment at 60° to 220°C.

[Embodiments of the Invention]

It is preferable to use split hide as a raw material of collagen in the present invention. Such split hide is obtained from fresh split hide or salted rawhide of slaughtered animals such as cows. Split hide comprises insoluble collagen fibers for the most part and used after cleaning reticulated flesh or removing salt added to prevent decay and deterioration.

The insoluble collagen fibers contain impurities such as lipid including glyceride, phospholipid or free fatty acid, and protein other than collagen such as glycoprotein or albumin. These impurities have great influence on spinning stability in forming fiber, qualities such as gloss, strength and elongation, and smell in the process of fiber spinning. Therefore, it is preferable to remove the above impurities previously by carrying out conventional leather treatment such as acid or alkali treatment, enzyme treatment or solvent treatment after disassembling collagen fibers by soaking the collagen fibers, for example, in lime to hydrolyze lipid in the insoluble collagen fibers.

The thus-treated insoluble collagen fibers are then subjected to solubilization treatment in order to cut the crosslinked peptides. As the process for solubilization treatment, generally known alkali solubilization processes or enzyme solubilization processes can be adopted.

In case of applying the alkali solubilization process, neutralization is preferably carried out by acid such as hydrochloric acid. Alternatively, a process disclosed in Japanese Examined Patent Publication No. 15033/1971 may be used as an improved method of conventionally known alkali solubilization processes.

The above enzyme solubilization process has an advantage that regenerated collagen having uniform molecular weight can be obtained, and can be suitably used for the present invention. As the enzyme solubilization process, it is possible to adopt processes described in Japanese Examined Patent Publication No. 25829/1968 and Japanese Examined Patent Publication No. 27513/1968. Furthermore, in the present invention, both of the above alkali solubilization process and the enzyme solubilization process may be employed together.

Collagen treated with the above solubilization process is preferably subjected to further treatment such as pH adjustment, salting out, water washing or solvent treatment, since regenerated collagen having excellent qualities can be obtained if such treatment is carried out.

The obtained solubilizable collagen is dissolved by using an acidic solution whose pH is adjusted to pH 2 to pH 4.5 with an acid such as hydrochloric acid, acetic acid or lactic acid to obtain a concentrate solution having a given concentration of, for example, about 1 to 15 % by weight, preferably about 2 to 10 %. If necessary, the obtained collagen aqueous solution may be subjected to defoaming with stirring under reduced pressure or filtration in order to remove water-insoluble minute contaminant. If necessary, a suitable amount of additives such as a

stabilizer and a water-soluble polymer compound may be added to the solubilizable collagen solution to be obtained for the purpose of increasing mechanical strength, enhancement of water resistance and heat resistance, development of gloss, improvement of fiber spinning properties, coloring prevention, corrosion proof, and the like.

The solubilizable collagen solution is discharged, for example, from a spinning nozzle or a slit and immersed into an inorganic salt aqueous solution to prepare regenerated collagen fibers. An aqueous solution of water-soluble inorganic salts such as sodium sulfate, sodium chloride and ammonium sulfate is used as the inorganic salt aqueous solution. Usually, concentration of these inorganic salts is adjusted to 10 to 40 % by weight. The pH of the inorganic salt solution is generally adjusted to pH 2 to pH 13, preferably pH 4 to pH 12 by adding, for example, a metallic salt such as sodium borate or sodium acetate, hydrochloric acid, boric acid, acetic acid, sodium hydroxide, and the like. In the case where the pH is less than 2 and the case where the pH is more than 13, there is a tendency that peptide bond in collagen is easily hydrolyzed and it becomes difficult to obtain the aimed fibers. The temperature of the inorganic salt solution is not particularly limited, but preferably at most 35°C in general. When the temperature is higher than 35°C, solubilizable collagen tends to be denatured, or strength of fibers to be obtained is lowered, making stable fiber spinning difficult. The lowest temperature is not particularly limited and suitably adjusted in accordance with the solubility of inorganic salt.

A suitable amount of additives such as a stabilizer and a water-soluble polymer compound may be added to the solubilizable collagen solution obtained in the above manner, if necessary, for the

purpose of increasing mechanical strength, enhancement of water resistance and heat resistance, development of gloss, improvement of fiber spinning properties, coloring prevention, corrosion proof, and the like.

In the present invention, the above regenerated collagen fibers are treated with a monofunctional epoxy compound or by immersion to solution thereof. Concrete examples of the monofunctional epoxy compound used in the present invention are olefin oxides such as ethylene oxide, propylene oxide, butylene oxide, isobutylene oxide, octene oxide, styrene oxide, methylstyrene oxide, epichlorohydrin, epibromohydrin or glycidol, glycidyl ethers such as glycidyl methyl ether, butyl glycidyl ether, octyl glycidyl ether, nonyl glycidyl ether, undecyl glycidyl ether, tridecyl glycidyl ether, pentadecyl glycidyl ether, 2-ethylhexyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, cresyl glycidyl ether, t-butylphenyl glycidyl ether, dibromophenyl glycidyl ether, benzyl glycidyl ether, polyethyleneoxide glycidyl ether, glycidyl esters such as glycidyl formate, glycidyl acetate, glycidyl acrylate, glycidyl methacrylate or glycidyl benzoate, glycidyl amides and the like. However, the present invention is not limited to these examples.

In the present invention, when treatment is conducted using the monofunctional epoxy compound represented by the following formula (I), water adsorption of the regenerated collagen fibers is lowered, thus being preferable



(wherein R indicates a substituent group represented by  $R_1$ -,  $R_2$ -O- or  $R_2$ -COO-,  $R_1$  in the substituent group indicates a hydrocarbon group having at least 2 carbon atoms or  $CH_2Cl$  and  $R_2$  indicates a hydrocarbon group having at least 4 carbon atoms).

Examples of the compound represented by the above formula (I) are butylene oxide, isobutylene oxide, styrene oxide, epichlorohydrin, butyl glycidyl ether, octyl glycidyl ether, glycidyl methacrylate and the like, but are not limited to these.

In particular, monofunctional epoxy compounds whose  $R_1$  in the above formula is hydrocarbon group having at least 2 to at most 6 carbon atoms or  $CH_2Cl$ , such as butylene oxide or epichlorohydrin, or monofunctional epoxy compounds whose  $R_2$  in the above formula is hydrocarbon group having at least 4 to at most 6 carbon atoms, such as butyl glycidyl ether or phenyl glycidyl ether, are preferably used from the viewpoints that treatment can be carried out faster due to high reactivity and that treatment in water is relatively easy.

The amount of the monofunctional epoxy compound used in the present invention is 0.1 to 500 equivalent, preferably 0.5 to 100 equivalent, more preferably 1 to 50 equivalent based on the amount of amino group in the regenerated collagen. When the amount of the monofunctional epoxy compound is less than 0.1 equivalent, insolubilization effect of regenerated collagen fibers against water is insufficient. On the other hand, the amount of more than 500 equivalent is unfavorable from the viewpoint of industrial handling or from an environmental point of view though insolubilization effect is satisfactory.

The monofunctional epoxy compound is used as it is or after

dissolving the same into various solvents. Examples of the reaction solvent are water, alcohols such as methyl alcohol, ethyl alcohol or isopropanol, ethers such as tetrahydrofuran and dioxane, organic halogenated organic solvents such as dichloromethane, chloroform and carbon tetrachloride, neutral organic solvents such as DMF and DMSO, and the like. A mixed solvent thereof may also be used. When water is used as the reaction solvent, an aqueous solution of inorganic salt such as sodium sulfate, sodium chloride or ammonium sulfate may be used if necessary. Usually, the concentration of these inorganic salts is adjusted to 10 to 40 % by weight. The pH of the aqueous solution may be adjusted by adding metallic salts such as sodium borate or sodium acetate, hydrochloric acid, boric acid, acetic acid and sodium hydroxide. In this case, the pH is preferably 6 to 13, more preferably 8 to 12. When the pH is less than 6, the reaction between epoxy group in the monofunctional epoxy compound and amino group in collagen slows down, making insolubilization against water insufficient. When the pH is more than 13, the effects tend to be the same and the peptide bonds of the collagen become susceptible to hydrolysis and obtaining the desired fibers becomes difficult. As pH tends to decrease with time, a buffer may be used if necessary.

The temperature for treating regenerated collagen fibers by using an epoxy compound is at most 50°C. When the treatment temperature is higher than 50°C, regenerated collagen fibers tend to be denatured and strength of the fibers to be obtained is lowered, making stable fiber spinning difficult.

In addition, various additives such as catalysts and reaction auxiliaries may also be used. Examples of the catalyst are amines and



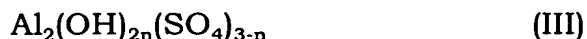
imidazoles. Concretely, examples of the amines include tertiary amines such as triethyl diamine, tetramethyl guanidine, triethanol amine, N,N'-dimethylpiperazine, benzyldimethyl amine, dimethylaminomethyl phenol and 2,4,6-tris(dimethylaminomethyl)phenol, secondary amines such as piperazine and morpholine, quaternary ammonium salts such as tetramethyl ammonium salt, tetraethyl ammonium salt and benzyltriethyl ammonium salt, and the like. Examples of the imidazoles include 2-methylimidazol, 2-ethylimidazole, 2-isopropylimidazol, 1-cyanoethyl-2-methylimidazol, 1-cyanoethyl-2-ethylimidazole, 1-cyanoethyl-2-isopropylimidazol, 2-ethyl-4-methylimidazol, and the like. Examples of the reaction auxiliary are salicylic acid or metallic salt of salicylic acid; thiocyanic acid salts such as thiocyanic acid and ammonium thiocyanate; tetramethylthiramdisulfide; thiourea; and the like.

In the present invention, the regenerated collagen fiber is subjected to water washing if necessary. Water washing has an advantage of removing inorganic salt which was mixed to the fibers during the fiber spinning process.

The above regenerated collagen fibers are then immersed into an aluminum salt aqueous solution in the present invention. According to this treatment, hardness can be imparted to regenerated collagen fibers even in wet conditions and wet touch of fibers is improved. Preferably, the treatment is carried out so that fibers after treatment contain 2 to 20 % by weight of an aluminum salt converted to an aluminum oxide basis.

The kind of aluminum salt used herein is not particularly limited but a basic aluminum salt having high reactivity with collagen is

preferable. Basic aluminum chloride and basic aluminum sulfate represented by the following formula (II) and (III) are more preferable:



(wherein n is 0.5 to 2.5).

Specifically, aluminum sulfate, aluminum chloride or alum is used. These aluminums may be used alone or in combination of two or more. The concentration of the aluminum salt in aqueous solution thereof is preferably 0.3 to 5 % by weight converted to an aluminum oxide basis. When the concentration of aluminum salt is less than 0.3 % by weight, regenerated collagen fibers tend to have a small aluminum content and wet touch of fibers becomes inferior. When the concentration is more than 5 % by weight, fibers after treatment are hardened, making it impossible to achieve favorable touch.

The pH of the aluminum salt aqueous solution is normally adjusted to pH 2.5 to pH 5 by using, for example, hydrochloric acid, sulfuric acid, acetic acid, sodium hydroxide, sodium carbonate or the like. When the pH is less than 2.5, there is a tendency that collagen structure is destroyed and denatured. When the pH is more than 5, aluminum salt precipitates and is hardly immersed into fibers. It is preferable to immerse an aluminum salt solution into regenerated collagen fibers with adjusting the pH to 2.2 to 3.5 at first, and then complete the immersion with adjusting the pH to 3.5 to 5 by adding sodium hydroxide or sodium carbonate. When an aluminum salt

having high basicity is used, it may be sufficient to carry out only the first pH adjustment of 2.5 to 5. The temperature of the aluminum salt solution is not particularly limited, but preferably at most 50°C. When the temperature of the solution is higher than 50°C, regenerated collagen fibers tend to be denatured.

The time to immerse an aluminum salt aqueous solution into regenerated collagen fibers is at least 3 hours, preferably 6 to 25 hours. When the immersion time is shorter than 3 hours, reaction of aluminum salt is difficult to proceed and water resistance of fibers is insufficient. Though there is no particular upper limit for the immersion time, reaction of aluminum salt proceeds sufficiently and water resistance becomes excellent within 25 hours.

In order to avoid uneven concentration by rapid absorption of aluminum salt into regenerated collagen fibers, inorganic salts such as sodium chloride, sodium sulfate and potassium chloride may be suitably added to the above aluminum salt aqueous solution. In order to improve stability of aluminum salt in water, an organic salt such as sodium formate or sodium citrate may be suitably added to the above aluminum salt aqueous solution.

The regenerated collagen fibers treated with aluminum salt are then subjected to washing in water, oiling and drying. Drying is preferably conducted at 100°C or lower, more preferably 75°C or lower.

Water washing is carried out at this stage in order to prevent oil precipitation due to salt, or to prevent generation of break in regenerated collagen fibers caused by the salt precipitated from the regenerated collagen fibers during the drying step in a dryer. In addition, water washing can prevent lowering of heat transfer coefficient

caused by the salt scattered and adhered to the heat exchanger in the dryer. When oiling is carried out, there are effects on prevention of sticking of fibers and improvement of surface properties thereof in dry conditions.

In the present invention, the regenerated collagen fibers of the present invention can then be curled as aimed, other shapes being easily imparted thereto and setting being carried out with maintaining the shape properly, by thermally setting the regenerated collagen fibers by means of hot water treatment at 20° to 160°C and heat drying treatment at 60° to 220°C. The hot water treatment means a thermal treatment performed in the presence of water. The treatment may include spraying mist adjusted to a pre-determined temperature by a spray, leaving the regenerated fibers in a water vapor environment adjusted to a pre-determined temperature or immersing fibers in water adjusted to a pre-determined temperature. For example, when treating in a temperature higher than 100°C, conducting treatment in an autoclave in a water vapor environment is preferable and all known methods may be used without limit.

Specifically, a preferable treatment is such that regenerated collagen fibers are fixed in a desirable shape (spiral shape and the like) with adjusting the temperature of the regenerated collagen fibers to 20° to 160°C in the presence of water. The temperature of the fiber is measured by inserting a thermocouple into the fiber bundle.

Though it is very difficult to determine the amount of water existing on the surface of the regenerated collagen fibers in case of treating fibers in the presence of water, it is preferable to distribute water on the surface almost uniformly so that the regenerated collagen

fibers are treated equally.

According to this treatment conducted in the presence of water, it becomes difficult to impart a desirable shape to regenerated collagen fibers when the temperature of the regenerated collagen fibers is too low. On the other hand, it is feared that the regenerated collagen fibers are deformed when the temperature of the regenerated collagen fibers is too high. It is desired that the treatment is carried out at temperature of usually 20° to 160°C, preferably 50° to 120°C, more preferably 70° to 110°C, and most preferably 80° to 90°C.

The time for hot water treatment is suitably determined in accordance with atmosphere and temperature adopted for treating regenerated collagen fibers. The fibers are usually treated for at least 5 minutes, preferably at least 15 minutes.

Secondly, the heat drying treatment means a treatment to put a fiber bundle into a hot air convection dryer or to carry out heating by applying hot air to the fibers using a dryer and the like, while any conventional process may be used without particular limitation. Specifically, it is preferable to carry out drying under air of 60° to 220°C with fixing fibers in a pre-determined shape after the hot water treatment.

When the temperature is lower than 60°C, it becomes difficult to impart a desirable shape to the regenerated collagen fibers. On the other hand, when the temperature is higher than 220°C, it is feared that regenerated collagen fibers are deformed and colored. It is desired that the treatment is carried out at a temperature of usually 60° to 220°C, preferably 90° to 160°C, more preferably 100° to 130°C, and most preferably 110° to 120°C.

The time for heat drying treatment is suitably determined in accordance with temperature for drying, the amount of fibers to be dried and the like. The fibers are usually treated for at least 5 to 120 minutes, preferably at least 10 to 60 minutes, more preferably 15 to 30 minutes.

According to these treatments, regenerated collagen fibers can be set to desirable shapes with maintaining those shapes properly.

As a process for fixing regenerated collagen fibers in a desirable shape previously, there is a process to wind regenerated collagen fibers along a pipe or a bar, a process to stretch regenerated collagen fibers between two or more supporting points, a process to clip regenerated collagen fibers between plates, and the like. Another process may be employed as long as the fibers are fixed in a desirable shape while water is supplied to the fibers sufficiently and the fibers can be dried at 60°C or more.

#### [Examples]

Hereinafter, the present invention is explained in more detail based on Examples, but the present invention is not limited thereto.

#### (A) Preparation of regenerated collagen fiber

A piece of cow split hide was subjected to solubilization treatment with alkali as a raw material and dissolved in an aqueous solution containing lactic acid to prepare a concentrate solution adjusted to pH 3.5 and collagen concentration of 6 % by weight. The concentrate solution was subjected to stirring and defoaming under reduced pressure. The solution was then transferred to a piston type concentrate solution tank for fiber spinning and kept under reduced pressure to carry out further defoaming. The concentrate solution was extruded, supplied in fixed quantities by using a gear pump and then

filtered through a sintered filter having a pore diameter of 10  $\mu\text{m}$ . The solution was discharged into a 25°C coagulation bath containing 20 % by weight of sodium sulfate (adjusted to pH 11 by boric acid and sodium hydroxide) through a spinning nozzle having a pore diameter of 0.35 mm, a pore length of 0.5 mm and a pore number of 50 at a spinning rate of 4 m/minute.

(B) Oiling agent treatment

The obtained fiber was washed with water and immersed in a bath filled with an oiling agent containing emulsion of silicones modified with amino group and a PLURONIC polyether antistatic agent to apply the oiling agent to the fibers.

EXAMPLE 1

Regenerated collagen fibers were obtained by the method described in (A).

Then, 42.6 equivalent of epichlorohydrin based on the amount of amino group in collagen was added to an aqueous solution containing 0.9 % by weight of 2,4,6-tris(dimethylaminomethyl)phenol, 0.09 % by weight of salicylic acid and 13 % by weight of sodium sulfate and the obtained regenerated collagen fibers were immersed into the solution at 25°C for 24 hours.

After an hour of washing by running water, the fibers were immersed in an aqueous solution containing 10 % by weight of basic aluminum chloride (Bellcotan AC-P available from Nippon Fine Chemical Co., Ltd. was used, used hereinafter in Examples and Comparative Examples) and 15 % by weight of sodium chloride at 25°C for 12 hours. Thereafter, the obtained fibers were washed by running

water for two hours. Then, oiling agent treatment was conducted by the method described in (B) and drying was carried out in the state of tension using a hot air convection dryer (PV-221 made by Tabai Espec Corporation was used, used hereinafter in Examples and Comparative Examples) adjusted to 70°C.

#### EXAMPLE 2

Experiment was carried out in the same manner as in Example 1 except for changing the monofunctional epoxy compound to phenyl glycidyl ether.

#### EXAMPLE 3

Experiment was carried out in the same manner as in Example 1 except for changing the amount of basic aluminum chloride (same as in Example 1, hereinafter the same) to 5 % by weight.

#### EXAMPLE 4

Experiment was carried out in the same manner as in Example 2 except for changing the amount of basic aluminum chloride to 5 % by weight.

#### EXAMPLE 5

Regenerated collagen fibers were obtained by the method described in (A).

Then, after adding epichlorohydrin in an amount of 42.6 equivalent based on the amount of amino group in collagen, the obtained regenerated collagen fibers were immersed in an aqueous



solution containing 0.9 % by weight of 2,4,6-tris(dimethylaminomethyl)phenol, 0.09 % by weight of salicylic acid and 13 % by weight of sodium sulfate at 25°C for 24 hours.

After an hour of washing by running water, the fibers were immersed in an aqueous solution containing 5 % by weight of basic aluminum chloride, 15 % by weight of sodium chloride and 1 % of sodium formate at 4°C for 12 hours. Thereafter, the obtained fibers were washed by running water for two hours. Then, oiling agent treatment was conducted by the method described in (B) and drying was carried out in the state of tension using a hot air convection dryer adjusted to 70°C.

#### COMPARATIVE EXAMPLE 1

Regenerated collagen fibers were obtained by the method described in (A).

Then, the obtained regenerated collagen fibers were immersed in an aqueous solution containing 10 % by weight of basic aluminum chloride and 15 % by weight of sodium chloride at 25°C for 12 hours. Thereafter, the obtained fibers were washed by running water for two hours. Then, oiling agent treatment was conducted by the method described in (B) and drying was carried out in the state of tension using a hot air convection dryer adjusted to 70°C.

#### COMPARATIVE EXAMPLE 2

Regenerated collagen fibers were obtained by the method described in (A).

The regenerated collagen fibers were insolubilized by

immersing in an aqueous solution of 25°C containing 15 % by weight of sodium sulfate and 0.5 % by weight of formaldehyde (adjusted to pH 9 by using boric acid and sodium hydroxide) for 15 minutes.

After an hour of washing by running water, the fibers were immersed in an aqueous solution containing 10 % by weight of basic aluminum chloride and 15 % by weight of sodium chloride at 25°C for 12 hours. Thereafter, the obtained fibers were washed by running water for two hours. Then, oiling agent treatment was conducted by the method described in (B) and drying was carried out in the state of tension using a hot air convection dryer adjusted to 70°C.

The thus-obtained regenerated collagen fibers were examined with regard to denier, aluminum content, forming of curl and curling characteristics according to the following method.

(Denier)

Denier was measured in an atmosphere adjusted to temperature of  $20 \pm 2^{\circ}\text{C}$  and relative humidity of  $65 \pm 2\%$  by using a denier measurement Denier Computer™ DC-77A (made by Search Co., Ltd.).

(Aluminum content)

After drying the regenerated collagen fibers in a desiccator, 0.1 g of the fibers were heated and dissolved in a solution obtained by mixing 5 ml of nitric acid and 15 ml of hydrochloric acid. The mixture was cooled and diluted fiftyfold with water to measure the aluminum content in the diluted aqueous solution by using an atomic absorption measurement equipment (Z-5300 type) made by Hitachi, Ltd. The aluminum content measured according to this method means the content of metal aluminum alone. The value was multiplied by 1.89 to

calculate the content of aluminum oxide.

(Forming of curl and measurement of curling characteristics)

Forming of curl and measurement of curling characteristics were carried out in the following manner.

(1) A fiber bundle opened sufficiently and adjusted to 130,000 denier (6.5 g/45 cm) was folded into two and tied with string. The bundle was trimmed off in the same fiber length at the point 20 cm from the knot.

(2) The fiber bundle was divided into four portions. Each portion was wound around an aluminum pipe having a major diameter of 12 mm and both ends of the bundle was fixed to the pipe by rubber bands to prevent the bundle from moving.

(3) The fiber-wound rod was then immersed in hot water adjusted to 80°C for 15 minutes to moisturize the fibers.

(4) The rod was taken from hot water and dried in a hot air convection dryer (PV-221 made by Tabai Espec Corporation) adjusted to 120°C for 15 minutes.

(5) Then, the rod was took out from the hot air convection dryer and cooled at room temperature for about 15 minutes to unwind the fiber bundle.

(6) As plain shampoo, the fiber bundle was washed by shaking 20 times in hot water of 40°C. The fiber bundle was taken out from hot water, and water on the surface was first wiped off by a towel and then removed by shaking. The bundle was hung up with keeping the spiral form, and curl length from the knot to the curl tip ( $C_p$ cm) without load and the length in case of stretching the curl ( $L_p$ cm) were measured, respectively. The bundle was then dried in the hot air convection dryer adjusted to 50°C.

(7) The dried fiber bundle was shampooed with combing 20 times in hot water adjusted to 40°C, containing 0.2 % of shampoo (Super Mild Shampoo/ Floral Fruity available from Shiseido Co. Ltd.). Light rinsing was carried out with rubbing under hot running water of 40°C. Water was removed in the same manner as in (6). Thereafter, the bundle was hung up with keeping the spiral form, and curl length from the knot to the curl tip ( $C_s$ cm) without load and the length in case of stretching the curl ( $L_s$ cm) were measured, respectively. The bundle was then dried again in the hot air convection dryer adjusted to 50°C.

(8) The procedure in (7) was repeated to evaluate shampoo resistance of the curl (curling percentage against the number of shampoo)

(9) Curling characteristics for evaluation were calculated in accordance with the following equations (IV), (V) and (VI).

Curling percentage immediately after plain shampoo ( $P_s$ )

$$P_s = (20 - C_p) \times 100 / L_p (\%) \quad (IV)$$

Curling percentage immediately after shampoo ( $Sc$ )

$$Sc = (20 - C_s) \times 100 / L_s (\%) \quad (V)$$

Curling retention immediately after shampoo ( $Ss$ )

$$Ss = (L_s - C_s) \times 100 / (L_s - C_p) (\%) \quad (VI)$$

Table 1 shows curling percentage after plain shampoo, curling percentage immediately after five shampoos and curling retention immediately after five shampoos as representative values.

TABLE 1

Sample No.	Denier	Aluminum oxide content (%)	Curling percentage after plain Shampoo (%)	Curling percentage immediately after five shampoos (%)	Curling retention immediately after five shampoos (%)
Ex. 1	67 d	12.5 %	28.2	20.5	70.0
Ex. 2	78 d	11.5 %	23.1	15.9	65.0
Ex. 3	61 d	10.5 %	28.2	19.5	66.0
Ex. 4	75 d	9.5 %	22.6	15.4	64.1
Ex. 5	65 d	11.2 %	28.3	19.7	67.1
Com. Ex. 1	63 d	13.5 %	17.9	5.1	16.7
Com. Ex. 2	64 d	13.0 %	23.1	5.1	12.5

The results in Table 1 show that it is possible to obtain fibers which has light color and excellent wet touch by treating regenerated collagen fibers with a monofunctional epoxy compound and aluminum salt. The results also show that it is possible to obtain fibers which can be formed into desirable shapes by keeping fibers at temperature of 20° to 160°C in the presence of water and then drying fibers at temperature of 60° to 220°C.

[Effect of the Invention]

The regenerated collagen fibers of the present invention have no color and excellent wet touch. In addition, the regenerated collagen fibers of the present invention can be formed into desirable shapes easily with the shape being maintained properly, and suitably used for curling hair ornaments such as wigs, hairpieces and doll hair or for shaping (setting) textile goods comprising woven fabrics or non-woven fabrics.

[Document Name] ABSTRACT

[Abstract]

[Problem] To provide regenerated collagen fibers which have no color and excellent touch in wet conditions and which can be formed into desirable shape with the shape being maintained properly.

[Solution] Regenerated collagen fibers are obtained by treating collagen with a monofunctional epoxy compound, and then treating the same with an aluminum salt in such a way that 2 to 40 % by weight of an aluminum salt converted to an aluminum oxide basis is contained to said collagen. The regenerated collagen fibers are thermally set by means of hot water treatment at 20° to 160°C and heat drying treatment at 60° to 220°C.

[Selected Figure] None